

# Theory of Chiral Imprinting

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We present a continuum model for a nematic elastomer network formed in a chiral environment, for instance in the presence of a chiral solvent. When this environment is removed, the network can retain some memory of its chiral genesis. We predict the residual chiral order parameter for a number of possible scenarios, and go on to examine the robustness (stability) of the imprinted chirality. We show that a twist-untwist transition can take place, which determines whether the imprinting has been successful. A transition is via a coarsening of the helical director pattern and a lengthening of its pitch. Finally, the effect due to a subsequent swelling by an achiral solvent, or by a solvent of differing chirality, is considered.

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Nematic elastomers combine the properties of a liquid crystal and those of a conventional rubber. This synergy gives rise to novel material behaviour, which in turn has stimulated much research in past years [1]. From a general symmetry argument, de Gennes [2] first suggested that chirality may be introduced to such an elastomer by simply forming it in a chiral solvent. The originally achiral liquid crystalline polymer would then remember the induced chirality after crosslinking, even when the solvent is removed or replaced with an achiral one. This is the case of chiral imprinting, which potentially can open up an entirely new way of producing materials of specified optical properties. Chiral imprinting, in principle, is akin to crosslinking a nematic polymer under an external magnetic or mechanical field [1,3] where the monodomain state is also permanently imprinted. Experimentally chiral imprinting was studied long ago [4] as a function of solvent exchange. Recently imprinting has been studied [5] as a function of both solvent removal and temperature. Another measure of imprinting occurs in intrinsically cholesteric networks. On temperature changes that would cause a substantial pitch variation in a non-crosslinked cholesteric polymer melt, the corresponding network suffers essentially no variation - see for example Fig. 8 of reference [6], where also many other references to cholesteric elastomers are given. In this paper, we analyse chiral imprinting, and predict the retained chiral properties of the elastomer when the initial chiral environment of crosslinking is altered. Gradients of director variation are modeled within continuum Frank nematic elasticity. The nematic elastomer penalty for rotation of the director relative to the solid matrix is described in a fully non-linear, rubber-elastic manner since rotation can be large.

A nematic liquid crystal has a mobile director  $\mathbf{n}$ , the gradient of which incurs a Frank energy [7]. For the free energy density of a cholesteric liquid crystal, the twist term is modified by a pitch wave number,  $q_0$ :

$$f_c = \frac{1}{2} [K_1(\nabla \cdot \mathbf{n})^2 + K_2(\mathbf{n} \cdot (\nabla \times \mathbf{n}) + q_0)^2 + K_3((\mathbf{n} \cdot \nabla) \mathbf{n})^2]$$

where  $K_{1,2,3}$  respectively measure the energy penalty for splay, twist and bend, the three possible modes of the nematic director distortion. In a pure twisting, cholesteric conformation of the director, we can drop the terms involving  $K_{1,3}$ . These other contributions arise if the director moves away from the helical plane and tilts toward the pitch axis. The Frank energy can be viewed as a continuum description with higher order spatial derivatives truncated, and it suffices for cases where director varies slowly over a nematic coherence length ( $\sim 10\text{nm}$ ).

When liquid crystalline polymers are crosslinked into a rubber network, additional constraints on  $\mathbf{n}$  arise in the form of director anchoring to the network. Anchoring manifests itself with an extra energy cost [8] for a uniform director rotation  $\omega$  relative to a local rotation of the elastic matrix  $\Omega$ . The energy density is  $\frac{1}{2} D_1 [(\Omega - \omega) \times \mathbf{n}]^2$ . A second term couples the relative director-matrix rotation to the shearing part of the elastic strain,  $\lambda$ , that is  $D_2 \mathbf{n} \cdot \lambda \cdot [(\Omega - \omega) \times \mathbf{n}]$ . For such strains to rotate the director in a cholesteric, they would have to vary along the helical axis. By the requirement of elastic compatibility this introduces secondary shears. One can show that these are prohibitively expensive for this geometry. We accordingly ignore  $\lambda$  terms.

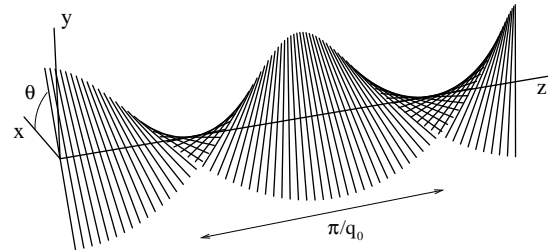


FIG. 1. A cholesteric director configuration.

Consider an initially regular cholesteric helix along the  $z$  axis, Fig. 1.  $\theta$  is the azimuthal angle the local director makes within the  $x - y$  plane and is initially

$$\theta_0(z) = q_0 z \quad (1)$$

where  $q_0$  is the chiral pitch wavenumber. One can generalise the  $D_1$  term to the large angle limit by considering a molecular nematic rubber elastic model [1]. It is no longer  $\frac{1}{2}D_1 (\theta - \theta_0)^2$  but  $\frac{1}{2}D_1 \sin^2(\theta - q_0 z)$  which has the correct locally nematic symmetry of  $\mathbf{n} \equiv -\mathbf{n}$ . The energy for an elastomer formed under a cholesteric solvent which is subsequently replaced with an achiral one is then:

$$F = \int dz \frac{1}{2} [K_2 \theta'^2 + D_1 \sin^2(\theta - q_0 z)] \quad (2)$$

where  $'$  indicates  $d/dz$ . The first term in  $F$  wishes to remove the twist in  $\mathbf{n}$  since now the chiral imperative of the solvent is removed the usual Frank twist penalty is fully incurred. However the second term insists that  $\mathbf{n}$  is anchored to a helix thanks to the crosslinks being formed under cholesteric conditions. The initial network polymers are taken to be achiral, thus  $q_0$  is only induced and can be tuned with the choice of the chiral solvent we subject our elastomer to at formation. If achiral solvent is used when crosslinking,  $q_0$  could simply be zero, and we retrieve the description of more conventional nematic elastomers [1].

The two limits of the energy density are (i) the perfectly twisted cholesteric state  $f = \frac{1}{2}K_2 q_0^2$  where the current pitch wavevector is unchanged from  $q_0$ , and (ii) the untwisted state  $f = \frac{1}{4}D_1$ , the additional factor of  $\frac{1}{2}$  arising from the averaging of  $\sin^2$  over one period. Thus, crudely, we expect the director to be twisted if

$$K_2 q_0^2 < D_1/2 \quad (3)$$

and untwisted otherwise, this balance being tuneable since  $K_2$ ,  $D_1$  and  $q_0^2$  vary relatively to each other with temperature, degree of crosslinking and swelling and the presence of additional chiral agents. Eq. (3) anticipates the physics of our detailed results: highly twisted states ( $q_0$  large) or systems with a large twist constant  $K_2$  will pay a very high Frank penalty on loss of spontaneous twist arising from the loss of the chiral solvent. A large combination  $K_2 q_0^2$  will overcome the anchoring  $D_1$  and the elastomer will untwist - imprinting will be lost. Weakly twisted elastomers with weak twist constants will not overcome director anchoring and imprinting will remain. We now analyze Eq. (2) for details of the phase behaviour.

To simplify matters, we begin with the following substitutions:

$$\phi = q_0 z - \theta + \pi/2; \quad u = z/\xi; \quad \xi = \sqrt{K_2/D_1}; \quad \alpha = \xi q_0$$

the angle  $\phi$  describes the variation away from (or modulation of) the original helical pattern, that is we are now in a rotating frame of reference. Lengths are reduced by the nematic rubber penetration depth  $\xi$ , the natural length scale in the problem. The parameter  $\alpha$  is a non-dimensional measure of the nematic length relative to the chiral pitch, and the condition (3) is equivalent

to  $\alpha \sim 1/\sqrt{2}$ . Following the remarks below Eq. (3), we expect imprinting to be lost at large  $\alpha$  and retained at small  $\alpha$ . Dropping a constant arising from the variable change  $\theta \rightarrow \phi$ , the reduced energy (per unit cross-section area perpendicular to the pitch axis) is:

$$\tilde{F} = \frac{2F}{D_1 \xi} = \int du [(\dot{\phi} - \alpha)^2 - \sin^2 \phi] \quad (4)$$

where  $(\dot{\phantom{x}})$  signifies  $d/du$ . If we make the analogy to Lagrangian dynamics, the integrand is the Lagrangian density ( $L = T - V$ ) of a particle in a potential given by  $\sin^2 \phi$ . The problem also now resembles the problem of an electric or magnetic field applied perpendicularly to the helix of a liquid cholesteric, solved long ago by de Gennes and Meyer [9]. In reduced terms, the  $\sin^2 \phi$  is like the field competing with the natural chirality  $\alpha$ . In terms of the original problem, Eq. (2), it is as if a naturally untwisted nematic has a spatially chiral electric field " $D_1$ " applied to it in an attempt to induce a twist.

The first integral of the Euler-Lagrange equation corresponding to Eq. (4), the elliptic equation or often called in the literature the Sine-Gordon equation, leads to:

$$\dot{\phi}^2 + \sin^2 \phi = c^2 \quad (5)$$

where  $c^2$  is the integration constant, which has the physical interpretation of total energy. The analogy is helpful, and before we examine the details we already foresee two scenarios: If  $c^2 < 1$ , the particle does not have sufficient energy to overcome the barriers in  $\sin^2 \phi$  potential and is therefore localized, *i.e.*  $-\pi/2 < \phi < \pi/2$ . This corresponds to the case where cholesteric pitch is largely maintained, with  $\phi(u)$  only introducing small modulations to the director orientation. If  $c^2 > 1$ , our particle can climb out of the potential valleys and travel freely; this corresponds to the case of winding/unwinding the cholesteric twists in director orientation. Below, we determine  $c$  in terms of  $\alpha$ .

*The localised limit,  $c^2 < 1$ .* Our particle oscillates between two values of  $\phi_m = \pm \arcsin c$ . We accordingly introduce a new variable  $\beta$  in the interval  $\beta \in [-\frac{\pi}{2}, \frac{\pi}{2}]$ , so that  $\sin \phi \equiv c \sin \beta$ . Rewriting the derivative  $\dot{\phi}$  in terms of  $\dot{\beta}$  and returning it to Eq. (5) reduces this equation to one of the standard elliptic form:  $\dot{\beta} = \sqrt{1 - c^2 \sin^2 \beta}$ . The period of the oscillatory motion is found to be:

$$T_1 = 2 \int_0^{\frac{\pi}{2}} \frac{d\beta}{\dot{\beta}} = 2 \mathcal{K}(c). \quad (6)$$

Here  $\mathcal{K}(c)$ , and later  $\mathcal{E}(c)$ , are the complete elliptic integrals of the first and second kind respectively. The period  $T_1$  gives, in units of the characteristic length scale  $\xi$ , the spatial repeat distance of our  $\phi$ -modulation of the original cholesteric angle  $q_0 z$ . The reduced energy of a period can be obtained from Eq. (4) as:

$$\tilde{F}_1(T_1) = 2[(c^2 + \alpha^2 - 2) \mathcal{K}(c) + 2 \mathcal{E}(c)]. \quad (7)$$

In order to compare the stability of various states, we require the reduced energy *density*. In the localized regime,  $c^2 < 1$ , we denote this by  $g_1(c)$ :

$$g_1 = \tilde{F}_1(T_1)/T_1 = c^2 + \alpha^2 - 2 + \frac{2\mathcal{E}(c)}{\mathcal{K}(c)}. \quad (8)$$

We now require the energy density in the traveling regime.

*The traveling limit*  $c^2 > 1$ . The modulation period down the original helix corresponds to the time taken for our particle to travel from one peak to the next in the potential. It is calculated using Eq. (5):

$$T_2 = 2 \int_0^{\frac{\pi}{2}} \frac{d\phi}{\dot{\phi}} = 2k \mathcal{K}(k) \quad (9)$$

where  $k = 1/c$ , and thus  $k < 1$ . The reduced energy of a period is:

$$\tilde{F}_2(T_2) = 2[(\alpha^2 - c^2)k \mathcal{K}(k) + 2c \mathcal{E}(k) - \alpha\pi]. \quad (10)$$

The corresponding energy density,  $g_2(c)$  for  $c^2 > 1$ , is:

$$g_2 = \tilde{F}_2(T_2)/T_2 = \alpha^2 - c^2 + \frac{2}{k \mathcal{K}(k)} \left[ \frac{\mathcal{E}(k)}{k} - \frac{\alpha\pi}{2} \right]. \quad (11)$$

Combining  $g_1(c)$  and  $g_2(c)$ , Eqs (8, 11), we now have the energy density  $g(c)$  for the entire range of  $c$ . Fig. 1 illustrates the energy density plots for three different values of the chiral strength, described by the parameter  $\alpha$ .

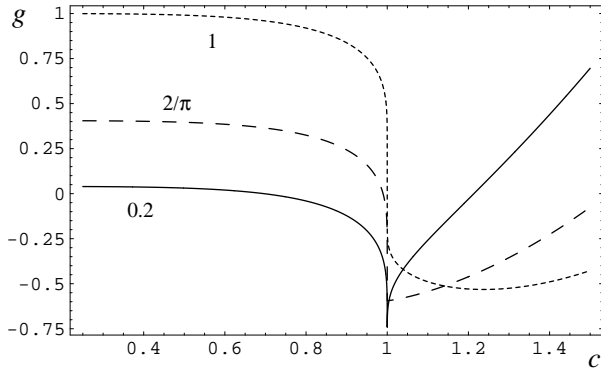


FIG. 2. Reduced energy density,  $g(c)$ , for  $\alpha = 0.2, 2/\pi, 1$ . One has  $g_1(c)$  for  $c^2 < 1$  and  $g_2(c)$  for  $c^2 > 1$ .

We can see that at the transition point  $c = 1$  the two energy densities approach each other. However, the densities are not smoothly joined, forming a cusp which turns from pointing downward to upward upon the parameter  $\alpha$  increasing past a critical value  $\alpha_c = 2/\pi$ . Invoking the identities for differentials of complete elliptic integrals:

$$\frac{d\mathcal{K}}{dk} = \frac{\mathcal{E}}{k(1-k^2)} - \frac{\mathcal{K}}{k} \quad ; \quad \frac{d\mathcal{E}}{dk} = \frac{\mathcal{E} - \mathcal{K}}{k}$$

we can minimise the reduced free energy with respect to  $k$ , or equivalently  $c$ , by setting  $dg/dc = 0$ . As evident from Fig. 2, minima only exist in the region  $c^2 > 1$ , that is in  $g_2(c)$ , and only when  $\alpha > \alpha_c$ . There are no minima in  $g_1$ . The analogous problem of a cholesteric liquid in the presence of an electric field [9] is similar. The condition  $dg/dc = 0$  fixes  $c$  since, for a given  $\alpha$ ,  $k$  or  $c$  must satisfy:

$$\alpha = \frac{2\mathcal{E}(k)}{\pi k} \quad \text{for} \quad \alpha > \alpha_c = 2/\pi. \quad (12)$$

The period of  $\phi(u)$  modulation is  $T = 2k \mathcal{K}(k)$  in units of  $\xi$ . For each such period along the helical pitch axis,  $\phi$  increases by  $\pi$ , the director unwinds once, and therefore one loses 1 of the  $T\xi q_0/\pi \equiv 2\alpha k \mathcal{K}(k)/\pi$  twists imprinted over the interval  $T$ . The imprinting efficiency is given by the fractional number of twists lost:

$$e_0 = \frac{2\alpha k \mathcal{K}(k) - \pi}{2\alpha k \mathcal{K}(k)}. \quad (13)$$

Provided that  $e_0$  is close to unity, much of the chirality can be preserved.

For small chiral power  $\alpha < \alpha_c = 2/\pi$ , the minimising condition  $dg/dc = 0$  has no solution and the minimum free energy occurs exactly at  $c = 1$ . The cusp has the energy density  $g = (2/\pi)^2 - 1$ , and a logarithmically divergent period  $T$  which implies  $e_0 = 1$ . The director gets arrested, attempting to untwist but never actually manages a full turn within a finite distance. The imprinting is therefore successful.

For chiral power  $\alpha > \alpha_c = 2/\pi$ , minima are found for  $c > 1$ . The period is no longer infinite and twists are lost. For large  $\alpha$ , *i.e.* the nematic penetration depth large compared to the cholesteric pitch, we can expand the elliptic function for small  $k$  to find  $\alpha \sim c(1 - k^2/4 - 3k^4/128...)$ . Alternatively  $k \sim 1/\alpha(1 - 1/4\alpha^2...)$  and we find a period of  $T = 2k \mathcal{K}(k) \sim \pi/\alpha$  in units of  $\xi$ . Thus for every actual distance of  $\pi\xi/\alpha = \pi/q_0$ ,  $\phi$  accumulates an increment of  $\pi$ . That is,  $e_0 \rightarrow 0$ , corresponding eventually to the case of complete unwinding of the imprinted helical pattern.

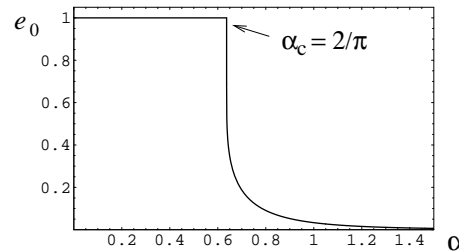


FIG. 3. Imprinting efficiency vs. network parameter  $\alpha$ . The slope at the critical point  $\alpha = \alpha_c^+$  diverges and the efficiency decays rapidly.

In writing equation (2), we have assumed that the chiral solvent was completely replaced with an achiral one as was the case in experiment [5]. However, we can trivially generalise  $F$  to the case where the current solvent is chiral:

$$F = \int dz \frac{1}{2} [K_2 (\theta' - q)^2 + D_1 \sin^2(\theta - q_0 z)] , \quad (14)$$

where  $q$  is the wave number that the solvent would introduce in the absence of crosslinks. Our previous case corresponds to  $q = 0$ . The mathematical procedure remains applicable, with an adjustment of the parameter  $\alpha = \xi q_0$  to:

$$\alpha' = \xi(q_0 - q)$$

which indicates a chiral environment of the same handedness can help preserve the chirality by reducing the value of  $\alpha$  (negative values of  $\alpha$  are mathematically equivalent to  $-\alpha$ , if we switch the sign of the  $\phi$  modulation). A chiral environment of the other handedness,  $q < 0$ , instead increases  $\alpha$  and has the opposite effect. It reduces imprinting, as one might expect. By simply varying  $q$ , via the solvent composition, we have a powerful way to map out the wind-unwinding transition.

Another interesting case is the induction of a cholesteric state in an initially uniform nematic network upon introducing a chiral solvent [10]. That is  $q_0 = 0$  and  $\alpha' = \xi q$ , where  $q$  is the chiral pitch wave number due to the chiral solvent. In this case,  $e_0$  given in Fig. 2 can be interpreted as the network resistance to imprinting - until the point  $\alpha'$  reaches  $2/\pi$  there will be no helicity induced in the network at all, and thereafter it rises with  $\alpha'$ .

Finally, by varying the amount of solvent in the crossed network, we can also tune, *i.e.* contract or expand, the volume relative to its original:  $V \rightarrow \beta V$ . With this, we expect from molecular interpretations,  $K_2 \rightarrow K_2$  for a special case where the local nematic order is preserved (the nematic order variation due to the solvent or temperature will be examined elsewhere), but  $D_1 \rightarrow D_1/\beta$  as it depends on crosslink density, and finally assuming an isotropic expansion/contraction,  $q_0 \rightarrow q_0 \beta^{-1/3}$ . Thus

we have

$$\alpha \rightarrow \alpha \beta^{1/6},$$

so swelling can, albeit weakly, increase the parameter  $\alpha$  in our model and discourage the preservation of the imprinted chirality.

In conclusion, we have proposed a continuum model for chiral imprinting in nematic elastomers. The model predicts the residual chirality when the chiral solvent is removed. A twist-untwist transition emerges from the theory, and an experimental verification of this transition would be a useful test of the theory presented here. Further work is focussed on the mechanical properties of networks; we expect an external mechanical field will have substantial influence on the imprinting of chirality.

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